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MECHANISMS FOR REMOVAL OF CARBON MONOXIDE FROM THE ATMOSPHERE

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SUMMARY

Theoretical and laboratory studies were performed, aimed at identifying significant removal processes of CO in the atmosphere. Three domains are considered in which the oxidation of carbon monoxide can occur: the stratosphere, the troposphere, and the oceans.

From theoretical considerations, the stratosphere is found to constitute a significant sink for CO on account of the reaction $OH + CO \rightarrow CO_2 + H$. Essentially all the CO entering into the stratosphere is thereby removed and the size of the stratospheric CO sink is given mainly by the transport rate of CO rich air through the tropopause into the stratosphere. It is concluded that the stratosphere removes 11 - 15 percent per year of the total CO inventory of the troposphere.

The major oxidant in the troposphere is ozone. Since a direct, bimolecular oxidation of CO by ozone constitutes a potential tropospheric CO removal mechanism, this reaction was investigated in the laboratory. It was found that the direct reaction was imperceptible, the upper limit of its rate coefficient being $k \leq 4 \times 10^{-25}$ cc/molecule sec. Accordingly, this reaction does not provide a significant sink for CO. It was found, however, that the oxidation of CO by ozone was catalyzed by methane which was present in the carbon monoxide as an impurity in the part per million range. Under the experimental conditions employed (which differed from tropospheric conditions) the catalyzed reaction was very fast. Since methane is a significant trace constituent in the troposphere, its concentration being 1.2 ppm, a catalyzed CO-oxidation by ozone may be an important process. The mechanism of the methane catalyzed CO oxidation is complex, comprising a chain reaction, and the total series of participating reactions is speculative. Therefore, it is not possible at present to evaluate the importance of this mechanism as a sink for CO in the troposphere.

In addition to atmospheric processes, the oceans provide a considerable oxidizing potential. Therefore, an exploratory experimental study has been made of CO oxidation in aqueous solutions by pH measurements. Since such a process of CO oxidation would have to be essentially catalytic in nature, and because of the extensive sedimentary ferromanganese depositions in the deep oceans, a heterogeneous catalysis with freshly precipitated colloidal iron hydroxide was considered a probable path for CO oxidation. However, the experiments did not indicate that this catalyst system was active in oxidizing CO. Instead, simple sodium chloride solutions of concentrations found in seawater were shown to promote the interaction of CO and oxygen. Although the formation of CO_2 in this system has not been demonstrated with the experimental techniques employed, it is shown to offer a reasonable interpretation of the observations.

I. INTRODUCTION

The increasing concern over the current high rate of carbon monoxide emission into the atmosphere -- at least partially from automobile exhaust -- has stimulated a search for the natural processes that are effective in removing CO from the atmosphere. In the absence of such processes, an accumulation of CO clearly should occur. A current estimate for the yearly global CO emission from anthropogenic sources rate is 200 million tons, corresponding to an atmospheric CO concentration increase of 0.05 ppm per year unless a portion of the carbon monoxide is scavenged. A variety of measurements performed over the past 20 years at locations remote from direct urban pollution have shown considerable short-time fluctuations of CO concentrations, but the average concentration levels seems to have remained essentially constant (see Table 1). Thus, it appears that one or more atmospheric CO removal processes are operative.

~~This~~ report presents results from laboratory and theoretical investigations directed at identifying chemical processes by which CO is oxidized and removed from the atmosphere. Three aspects are discussed: (a) the photochemical CO oxidation in the stratosphere; (b) reaction of CO with ozone in the troposphere; and (c) CO removal by oxidation in the hydrosphere. ~~In Section II~~ the mechanism of stratospheric CO removal is considered, and its significance as an atmospheric CO sink is discussed. ~~Section III gives~~ an account of a laboratory investigation of the reaction between CO and ozone. ~~Section IV describes~~ an exploratory experimental study of CO oxidation in aqueous solutions. ~~Finally, in Section~~ V, a summary is given of the conclusions drawn from these investigations with regard to atmospheric CO removal processes.

TABLE 1

ATMOSPHERIC CO CONCENTRATION MEASUREMENTS

Observer	Location	Year	Concentration (ppm)
Benesch et al. (1953)	Jungfraujoch	1950-1051	0.031-0.14
Locke and Herzberg (1953)	Ottawa	1952	0.11-0.22
	Ohio		0.19
	Jungfraujoch		0.15
	Mt. Wilson		0.16
Shaw (1958)	Columbus, O.	1952-53	0.13
Shaw (1959)	Columbus, O.	1959	0.04-2.2, average 0.11
Robbins et al. (1968)	Camp Century, Greenland	1965	0.24-0.90
	North coast, Calif.	1965	0.8
	Crater Lake, Ore.	1965	0.03-0.3
	Patrick Pt. Calif.	1965	0.04-0.8
Robinson and Robbins (1968)	North Pacific	1967	0.03-0.8
Cavanagh et al. (1969)	Pt. Barrow, Alaska	1967	0.06-0.12, average 0.10
Robinson and Robbins (1969a)	Inge Lehmann Station, Greenland	1967	0.05-0.7 0.11 background average
Robinson and Robbins (1969b)	Southern Pacific	1968	0.06 (variable)

Note: the first four entries from Junge (1963a).

II. THE STRATOSPHERE AS A CHEMICAL SINK FOR CO

The most abundant chemically active entity in the stratosphere is ozone. Although laboratory experiments have shown that ozone can oxidize CO, the reaction appears to proceed predominantly by catalysis with hydrocarbons (see Section III). Clearly, the oxidation of CO by ozone is not restricted to the stratosphere, but would proceed also in the troposphere because of the considerable seepage of ozone downward through the tropopause. The tropopheric oxidation of CO will be discussed separately and is the subject of the next section. In the stratosphere, the oxidation of CO by ozone can be neglected because the competing reaction

$$OH + CO \rightarrow CO_2 + H \qquad (1)$$

is found to be very effective, so that essentially all the CO entering the stratosphere is consumed by OH radicals, even though their concentration is much less than that of ozone.

The quantitative aspects of the stratospheric CO removal were treated in detail in the sixth monthly progress report, and have been published in the literature (Pressman and Warneck, 1970). Hence, only the most pertinent factors will be discussed here, and a complete elaboration will not be made. Among the most important factors required to evaluate the effectiveness of the stratospheric CO sink are the CO source strength and the rate of transport of tropospheric air into the stratosphere. Their numerical values are still only approximately known. The current amount of anthropogenic CO emission into the atmosphere has been estimated as 200 million tons/year, stemming mainly from automobile exhaust (Jaffe, 1966; Robinson and Robbins, 1969b). Natural sources exist also, specifically biological ones, but their total size is not known at present (Junge and Seiler, 1969; Swinnerton, et al, 1969). The air exchange rate across the tropopause has been assessed from the residence time of air in the stratosphere, the rate of downward transport of ozone, and from meteorological studies. The value derived from the available data is $\sigma = 7.8 \times 10^{16}$ molecules/cm^2/sec, with an uncertainty of a factor of two (Pressman and Warneck, 1970). These values will be used in the discussion below.

The mechanism of stratospheric CO removal by reaction (1) may be considered in more detail. The presence of OH radicals in the ozonosphere results from the interaction of photochemically generated, excited oxygen atoms with water vapor. The effects of moisture upon the ozonospheric photochemistry has been studied recently by Hunt (1966) and by Leovy (1969). The photochemical mechanism is complex and involves a variety of species which could conceivably react with CO. However, only reaction (1) will be considered here because OH appears to be the most efficient CO oxidant. Reaction (1) is relatively fast. At 217^{o}K, the temperature prevailing in the lower stratosphere, the rate coefficient is $k_1 = 1 \times 10^{-13}$ cm^3 molecule^{-1}

sec^{-1} (Schofield, 1967). Nevertheless, the rate of destruction of OH radicals by (1) is estimated to be less than that due to other reactions in the photochemical mechanism, so that the OH concentrations are not greatly perturbed. The H atoms produced in (1) are very rapidly ($\approx 10^{-4}$ sec) converted to HO_2 by attachment to oxygen. Leovy (1969) has shown that the ratio of OH and HO_2 radical concentrations adjusts to a steady state within less than $\tau = 100$ sec. The supply rate of OH then is $\bar{n}_{OH}\,\Delta z/\tau \geq 10^6 \times 9 \times 10^5/10^2 \geq 9 \times 10^9$ molecules cm^{-2} sec^{-1}, where $\bar{n}_{OH}$ is the approximate average OH concentration in the altitude region $\Delta z = 9$ km above the tropopause. This supply rate is greater than the rate of transport of CO into the stratosphere from the troposphere (unless the fractional CO concentration exceeds 0.12 ppm and/or the air exchange rate across the tropopause is significantly larger than that given above). Therefore, an adequate supply of OH radicals for the oxidation of CO in the stratosphere is provided. If it is assumed that reaction (1) is the predominant CO loss reaction, the average fractional concentration of CO in the stratosphere, f*, is governed by

$$\frac{df^*}{dt} = -(1/2)\, k_1 f^* \left(\int_{strat} n_{OH} n\, dz \right) \Big/ N_s + \left(\frac{\sigma}{N_s}\right)(f - f^*) \qquad (2)$$

Here, n_{OH} is the number density of OH, n the total number density, both being functions of the altitude z, $N_s = \int_{strat} n\, dz$ is the total square centimeter column count of the number density in the stratosphere, f the fractional CO concentration in the troposphere, and $\sigma = 7.8 \times 10^{16}$ molecules cm^{-2} sec^{-1} is the atmospheric flux entering the stratosphere through the tropopause. The factor 1/2 in the second term takes into account that photochemical OH generation occurs only during the day and that at night the OH concentration reduces substantially. The integration is performed over the 11-20 km altitude domain, so that $N_s = 3.6 \times 10^{24}$ molecules cm^{-2}. Steady-state concentrations of OH were calculated by Leovy (1969) and by Hunt (1966) only at altitudes > 15 km. For the lower altitude regime, we have applied an extrapolation to the published data. The number densities employed in the evaluation of the integral and their products are shown in Table 2 for several altitudes. The product of the two number densities is essentially constant $n_{OH} \times n = 4.8 \times 10^{24}$, so that the computation of the integral is facilitated. The time constant for the depletion of CO is

$$\tau_r = 2N_s/k_1 \int_{strat} n_{OH} n\, dz = 1.7 \times 10^7 \text{ sec},$$

or about a half-year. Since the time constant of the reaction is of the same order as the time required for vertical mixing of air in the lower

TABLE 2

NUMBER DENSITIES FOR OH (AFTER LEOVY), TOTAL NUMBER DENSITIES (U. S. STANDARD ATMOSPHERE), AND THEIR PRODUCTS FOR THE LOW STRATOSPHERE

Altitude (km)	n_{OH} (10^6 Molecules cm^{-3})	n (10^{18} Molecules cm^{-3})	OH x n (10^{24} Molecules^2 cm^{-6})
11.0	0.60	7.60	4.56
12.5	0.80	6.00	4.80
15.0	1.20	4.06	4.88
17.5	1.80	2.74	4.92
20.0	2.60	1.85	4.82

stratosphere, a reasonably uniform CO mixing ratio will be established and a balance is achieved between the consumption of CO and its supply through the tropopause. Thus, $df^*/dt = 0$, and the ratio of the CO concentration in the stratosphere to that in the troposphere is

$$\frac{f^*}{f} = \sigma/N_s \Big/ \left(\frac{1}{\tau_r} + \frac{\sigma}{N_s}\right) = 0.26.$$

The net flux of CO into the stratosphere is given by

$$\sigma\,(CO) = \sigma f\,(1 - \frac{f^*}{f}) = 5.8 \times 10^{16} f \qquad (3)$$

(molecules $cm^{-2} sec^{-1}$)

To determine the significance of this process, it may be assumed that it provides the only CO sink in the atmosphere. If CO production and losses have achieved a steady state, and if the CO production rate is $P = 2 \times 10^8$ tons per year = 2.7×10^{10} molecules cm^{-2} sec^{-1} (Jaffe, 1968), one obtains for the tropospheric CO concentration

$$f = \frac{P}{\sigma} \Big/ (1 - \frac{f^*}{f}) = 4.7 \times 10^{-7}.$$

Comparison of this value, 0.47 ppm, with the measured tropospheric CO concentrations (Table 1) shows that the calculated CO concentration is 3-4 times greater than the observed concentration averages. Nevertheless, the similarity of magnitude indicates that the stratospheric CO removal medium discussed here provides a significant sink for CO.

The ratios of CO concentration in the stratosphere to that in the troposphere have been observed recently by Seiler and Junge (1969) and are, on the average, smaller than the value $f^*/f = 0.26$ derived here, indicating a more efficient CO consumption in the stratosphere than Equation (2) and Table 2 imply. The difference may be due to an inadequate photochemical theory, to the influence of circulation in the lower stratosphere which would increase the OH concentrations, or to additional reactions oxidizing CO. Some of the reaction rate coefficients employed by Leovy (1969) and Hunt (1966) require revision due to recent laboratory data. Two of the most important reaction rates [for $O(^1D)$ with nitrogen and water vapor] have changed by more than an order of magnitude, but their ratio has changed by only a factor of 2. Since in the model the equilibrium OH concentration is proportional to the 1/3 power of the ratio of rate coefficients, the changes of values causes a negligible effect. Snelling and Hampson (1969) have reviewed such factors critically and have concluded that below 40 km, the calculations of Leovy provide an adequate description of the atmospheric photochemistry. No assessment

appears to have yet been made of the downward transport of OH into the lower stratosphere, but the increase of OH concentration due to this effect would not be sizable. On the other hand, moist ozone photochemistry predicts the presence of species other than OH which may oxidize CO. For example, HO_2 radicals and H_2O_2 are predicted with concentrations orders of magnitude greater than that of OH. The reactions

$$HO_2 + CO \rightarrow CO_2 + OH \qquad (4)$$

$$H_2O_2 + CO \rightarrow CO_2 + H_2O \qquad (5)$$

are conceivable but no information is available at present on their rates.

While these factors are important in describing the details of CO oxidation in the stratosphere, it has been shown here that the OH + CO reaction consumes most of the carbon monoxide entering the stratosphere. Hence, the uncertainty of the size of the stratospheric CO sink is determined more by the uncertainty in the transport of air across the tropopuase than by additional reactions in the stratosphere.

The time constant for CO removal from the troposphere by transport to the stratosphere is, from Equation (3)

$$K_s = 3.15 \times 10^7 \, \sigma \, \frac{(1 - f^*/f)}{N_T} = 0.11 \text{ year}^{-1}$$

where $N_T = 1.66 \times 10^{25}$ is the cm^2 column number density of the troposphere and use is made of the fact that 1 year = 3.15×10^7 seconds. If the return flux of CO from the stratosphere is negligible, $K_s \simeq 0.15$. Accordingly, the average residence time of CO in the troposphere would be 7-9 years. Weinstock (1969) using a method based on the production of radioactive carbon in the atmosphere, has recently estimated the lifetime of CO in the atmosphere as 0.1 year. This value is probably too low because radioactive CO is produced mainly in the stratosphere, where it is converted to CO_2, and only a portion of it can be transported into the troposphere. Nevertheless, if the natural residence time of CO in the troposphere is as short as 0.1 year, it is clear that the stratosphere contributes only negligibly to the total CO removal from the atmosphere. On the other hand, if the residence time of CO is calculated from the estimated anthropogenic emission rate and the prevalent atmospheric CO concentration level (Table 1), a residence time of 2.7 years is deduced. Thus, even if natural sources are not important in comparison with the anthropogenic source, the stratospheric sink would contribute only partially to the overall CO removal rate. However, this conclusion depends on the assumption that a balance is achieved between CO production and

consumption. In fact, the CO emission from combustion sources has been rising almost proportionately with the automobile population, which has increased essentially linearly over the last 20 years, so that the assumption of a balance between CO production and removal from the atmosphere is not justified.

Since the strength of the natural CO sources is not known, it was considered important to investigate the influence of a variable CO emission rate upon the atmospheric CO concentration, by means of a general model study assuming a constant atmospheric sink. The details of this investigation have been published elsewhere (Pressman and Warneck, 1970). Briefly, the analysis provides several constraints for the rate of atmospheric CO removal compatible with the available data, including (1) the absolute CO concentration levels; (2) the ratio of CO concentrations in the Northern and Southern hemispheres; and (3) the temporal behavior of these parameters. The second of these is particularly noteworthy as it predicts a CO concentration gradient from the Northern to the Southern hemisphere on account of the much higher anthropogenic CO emission rate in the North. Indeed, a concentration ratio $f_N/f_S = 2$ has been measured by Robinson and Robbins (1969b) and a smaller one more recently by Junge and Seiler (1969). This would indicate that anthropogenic sources are significant in comparison with natural sources. In general, it has been found, however, that the derivation of a reliable value for the atmospheric rate of CO removal from the model study is precluded due to the present uncertainties in the measured CO concentrations and source function estimates. Hence, it can be concluded only, that the stratosphere removes 11-15 percent per year of the total CO inventory of the troposphere, but no conclusion is presently possible concerning the fractional contribution of the stratospheric sink to the total CO removal rate.

III. CO OXIDATION IN THE TROPOSPHERE

One of the principal oxidants in the atmosphere is ozone. It is generated in the higher stratosphere by photochemical processes and is brought down into the troposphere by an air exchange mechanism across the tropopause or tropopause gaps. It is destroyed in clouds, by trace substances and primarily by contact with the earth's surface. The resulting steady state tropospheric ozone concentration is about 40 micrograms per cubic meter, or about 5×10^{11} molecules/cm^3 at a constant mixing ratio. Harteck and Dondes (1957) have shown in laboratory experiments that CO is oxidized by ozone in a relatively slow reaction. The pertinent reaction mechanism has not been detailed, but at the temperatures employed by these investigators, 35 - 258°C, the oxidation by oxygen atoms seems to have played a major role. No conclusive results were obtained about the direct reaction

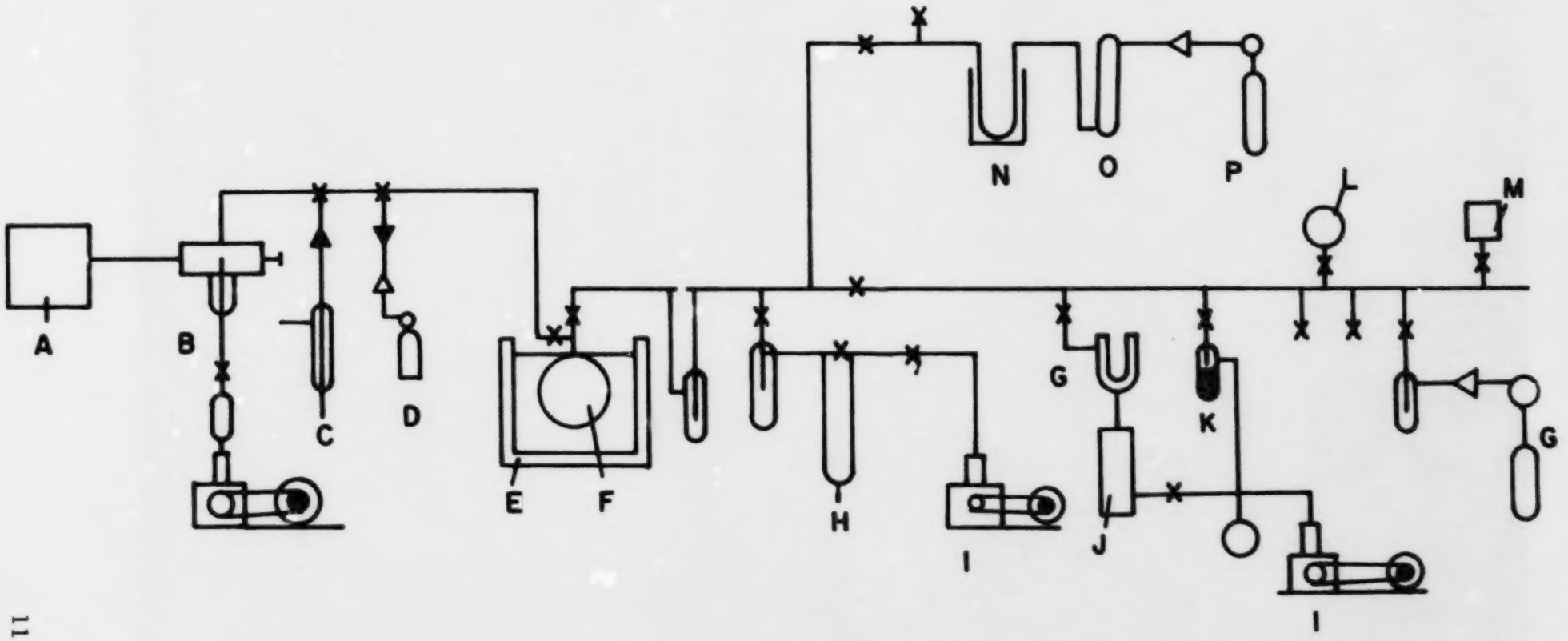
$$O_3 + CO \rightarrow CO_2 + O_2 \qquad (6)$$

Since at tropospheric pressures and temperatures, oxygen atoms cannot be a major agent for the direct oxidation of carbon monoxide, reaction (6) becomes an interesting possibility. Accordingly, it was considered important to study the rate of this reaction in the laboratory so that its significance in the atmosphere could be assessed. The results of this investigation are described in this section.

A. APPARATUS AND EXPERIMENTAL PROCEDURE

The reaction was studied in a 12 liter Pyrex flask. The large volume of the flask enabled removal of small samples (~3cc) of the reaction mixture for analysis without depleting the contents of the flask. Since ozone undergoes heterogeneous decomposition, the choice of a large volume of the reaction vessel (Surface to volume ratio = 0.21) minimized surface reactions and favored homogeneous gas phase reactions. The flask was submerged in a constant temperature bath contained in a 30 gallon polyethylene tank insulated with fiber glass. Temperature control was provided by a constant flow portable cooling unit which provided temperatures from ambient to -20°C. All the experiments, however, were performed at 23°C. The reduced temperature capability of the set-up was not fully utilized, because the results of the first experiments showed -- aside from complexities to be described later -- that the direct bimolecular reaction between ozone and CO did not proceed at a measurable rate even at room temperature.

The complete apparatus including the gas handling and analytical facilities in addition to the reaction vessel is shown in Figure 1. A conventional mercury free high vacuum line is employed for evacuation. It consists of a mechanical pump, and a 10 liter oil-diffusion pump



	Stopcock	G	Cold Trap	O	Ozone Generator
	Needle Valve	H	H_2SO_4 Manometer	P	Tank of Oxygen
A	F&M 700 Gas Chromatograph	I	Mechanical Pump		
B	Gas Sampling Valve	J	Diffusion Pump		
C	Ozone Absorber	K	Zeolite Turnings		
D	Nitrogen Tank	L	Wallace Tiernan Gauge		
E	Insulated Bath	M	Phillips Gauge		
F	12-liter Reaction Flask	N	Silica Gel Trap		

Figure 1. Outline of apparatus for ozone-carbon monoxide reaction study.

equipped with a liquid nitrogen cooled trap. High vacuum stop cocks were greased with Kel F grease which is resistent to attack by ozone. The line through which ozone was admitted to the reaction vessel as well as the vessel itself were fitted with unlubricated glass-teflon stopcocks. Traps filled with zeolite were placed in the pump line to the mechanical pumps in order that the direct interaction between ozone and pump oil was avoided when ozone was to be pumped from the manifold. For the same reason, a glass to metal bellows section replaced the usual rubber hose connections to the pumps. Residual gas pressure was measured with a cold cathode type ionization gauge. The vapor pressure of ozone was determined with a sulfuric acid manometer, that of all other gases was measured with a Bourdon-type gauge. For analysis, a sample of the gas mixture contained in the reaction vessel was drawn into an evacuated line, about 3cc in volume. The sample line was connected to the inlet valve of a gas chromatograph equipped with a thermal conductivity detector. A portion of the sample line could be isolated with two three way stopcocks. An inert carrier gas forced the sample thus trapped to bubble slowly through a reagent solution in which ozone was quantitatively absorbed. A 1 percent solution of sodium diphenylamine sulphonate acidified with perchloric acid was used as the absorber for ozone, since it has been shown to be sufficiently sensitive and yet less subject to interference than the customary potassium iodide solution (Bovee and Robinson, 1961). The optical absorption at 590 millimicrons resulting in the solution from the interaction with ozone was measured in a double beam spectrophotometer, and used to calculate the change in concentration of ozone. The gas chromatograph was equipped with a 6 foot x 1/8 inch column of molecular sieve 5A which separated O_2, N_2, CO and CO_2 in about 15 minutes time, when temperature programming was employed. The necessary calibrations of sensitivity were performed periodically.

Ozone was generated from oxygen flowing through an ozonizer and was stored in a trap filled with silicagel and subjected to dry ice temperature. The ozonizer consisted of a double-walled cylindrical container whose inner volume was filled with copper sulfate solution and whose outer surface was covered with aluminum foil. The $CuSO_4$ solution and the foil were wired to a 15,000 volt neon transformer. After a sufficient amount of ozone had been generated, the oxygen flow was shut off, the ozone generator line was isolated by closing two stopcocks, and the excess oxygen was pumped off via the gas handling manifold. Subsequently, the dry ice bath under the ozone trap was lowered to permit the evaporation of ozone into the reaction vessel. The stopcock connecting the sulfuric acid manometer was not opened until several minutes later, when the O_3 vapor pressure was sufficient to prevent the back diffusion of conceivable impurity vapors from the manometer line. Initial ozone pressure in the vessel varied between 3 and 25 Torr. The range of partial pressures of carbon monoxide was similar.

The carbon monoxide used in this work was of research grade quality. This is the highest grade available commercially and was acquired in a small steel tank at about 1000 lbs. pressure. Other gases used were oxygen, nitrogen, helium, hydrogen, methane, carbon dioxide. Of these, oxygen and nitrogen were of standard purity (99.9 percent minimum), helium was of the purity required for gas chromatography, and the others were of research grade quality.

B. RESULTS

The very first experiment demonstrated the unusual behavior of the reactive system. When carbon monoxide was admixed to ozone in the reaction vessel a fast reaction occurred during the process of mixing. The reaction was indicated by a bluish flash of chemiluminescence, and by the decrease of reactant concentrations as well as the formation of CO_2, identified by the subsequent gas chromatographic analysis. In contrast to the rapid reaction taking place during mixing, the resulting reactant product gas mixture appeared to be stable and no further reaction could be discerned. This behavior is shown in Figure 2, where the reactant and the CO_2 concentrations are plotted as a function of time over a period of seven days. Actually, a small decrease of the ozone concentration is observed, but it is not greater than that expected due to thermal decomposition. For comparison, Figure 3 shows the decrease of concentration of pure oxone over a similar period of time.

The unusual behavior of the reaction system demonstrated in Figure 2 has been observed in essentially all subsequent experiments. It may be caused by two conceivable mechanisms: (a) the presence of an impurity could give rise to a reaction with ozone, causing the catalytic oxidation of CO; and (b) the products from the direct reaction between ozone and carbon monoxide inhibit the reaction and cause it to cease after a sufficient amount of product is formed. A third possibility, the attainment of thermodynamic equilibrium does not apply here, because the equilibrium values of reaction (6) lie far to the right and either the ozone or the CO, or both should be almost completely consumed. On the basis of these arguments, a series of experiments were performed designed to determine whether (a) the fast initial reaction is caused by an impurity, or whether (b) it is a genuine reaction between ozone and CO subsequently inhibited by product formation. It should be noted here that the only products observed in all experiments were oxygen and carbon dioxide. However, only the CO_2 concentration could be measured in a quantitative manner whereas that of oxygen was falsified by the decomposition of ozone in the inlet system of the gas chromatograph.

The results of all experiments are summarized in Table 3 which gives the initial and final partial pressures of the reactants and the products. The resulting pressure differences are indicated. Also noted are the presence of other gases, and comments on the experimental conditions. The individual runs will not be discussed.

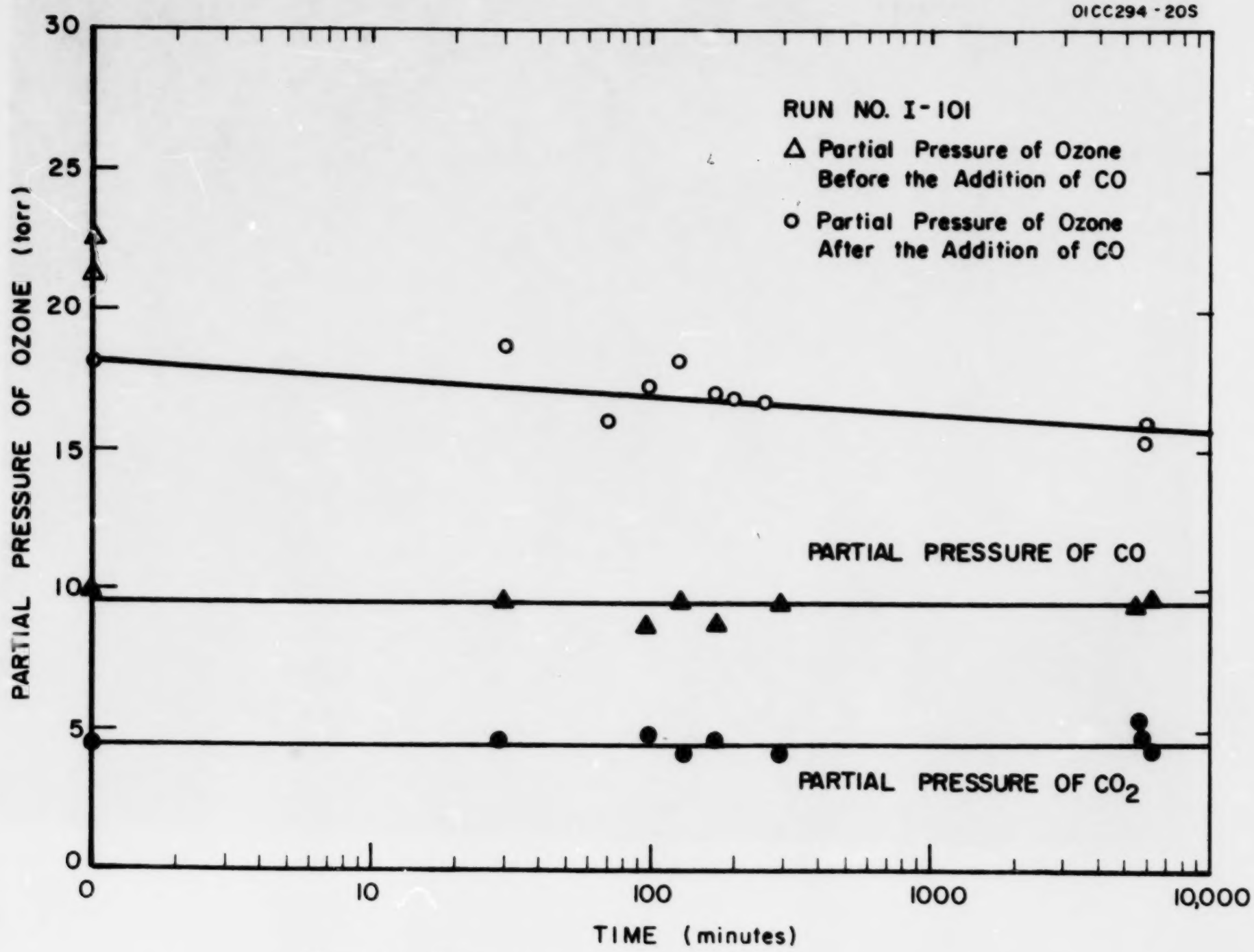


Figure 2. Change of reactant and product partial pressure with time.

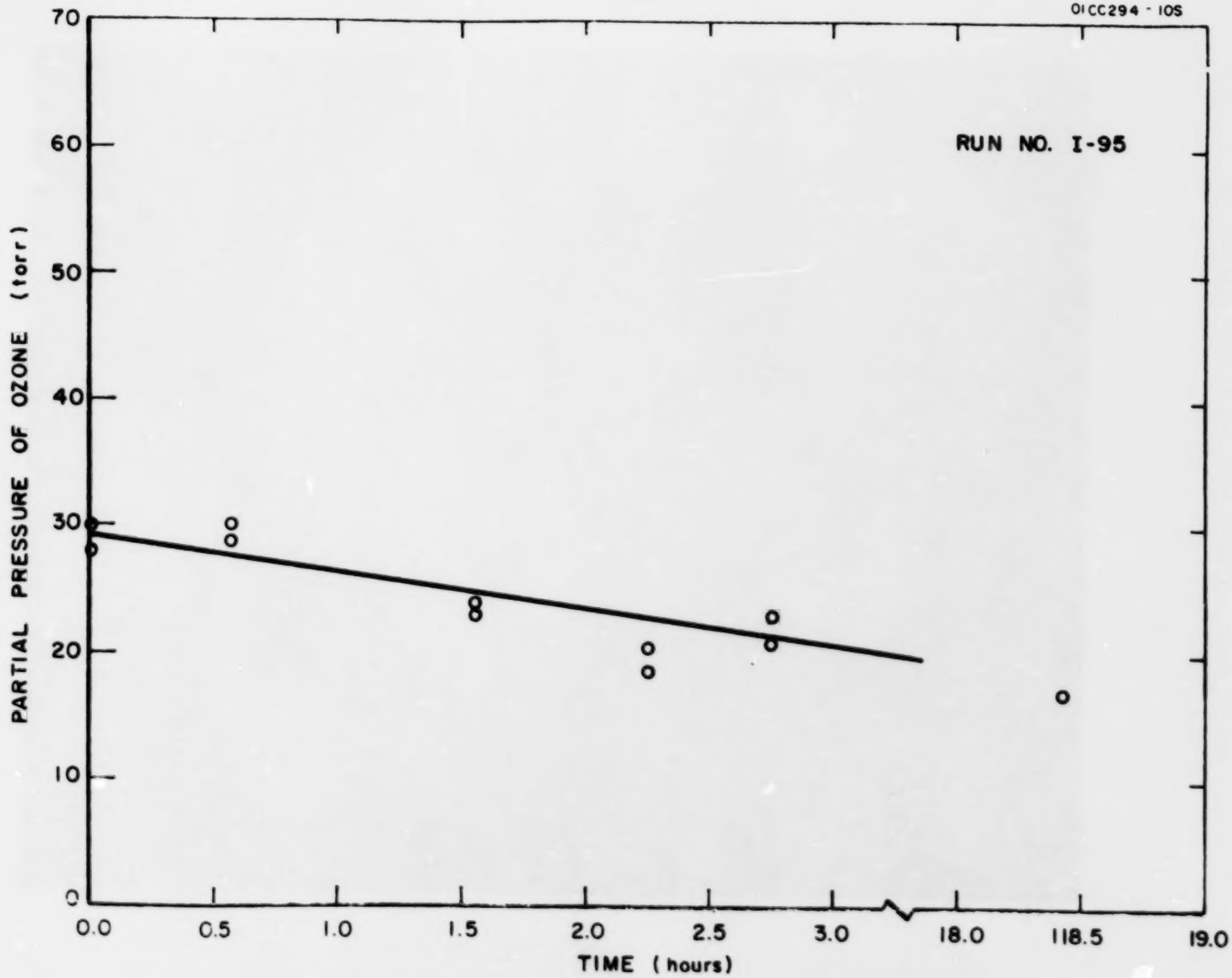


Figure 3. Change in ozone pressure with time.

TABLE 3

RESULTS OF CARBON MONOXIDE-OZONE EXPERIMENTS

RUN NO.	INITIAL PRESSURE OF REACTANTS (Torr)			FINAL PRESSURE OF COMPONENTS (Torr)			REACTANT PRESSURE DIFFERENCE		
	O_3	CO[1]	X[2]	O_3	CO	CO_2	ΔO_3	ΔCO	
I-101	22.0	Not Known	-	17.3	10.0	4.6	4.7	-	CO from tank thru Tygon tubing. Flash.
I-107	2.7	Not Known	-	0.5	13.1	1.7	2.2	-	Connect CO tank with glass tubing. Slow addition of CO, No flash.
I-111	14.8	12.4	-	9.7	10.3	1.6	5.1	2.1	Flash.
I-113	14.7	16.0	-	9.6	11.8	4.0	5.1	4.2	Flash.
I-114	13.6	11.5	N_3=30	8.9	7.2	4.7	4.7	4.3	N_2 - CO Mixture added to O_3. No flash.
I-115	15.8	34	CO_2=14.8	$\leq$ 0.9	31	17.3	$\geq$15.0	3.0	Intense flash.
I-118	12.8	16	-	2.9	11.5	2.8	9.9	4.5	Special precaution taken to eliminate traces of H_2O. Flash
I-125	30.7	Not Known	-	< 0.2	30	N.D.	30.5	-	Flash.
I-128A	16.3	22.3	-	6.4	14.3	7.75	9.9	8.0	Slow addition of CO. No flash.
B	6.4	20.0	CO_2=6.8 O_2 =10.0	4.4	17.0	9.75	2.0	3.0	Further addition of CO to gas mixture. Flash.
I-130A	23.3	18.2	-	15.7	11.4	6.7	7.6	6.8	No flash.
B	15.7	15.3	CO_2=6.7 O_2 ≈8	11.8	13.9	8.4	3.9	1.4	Slow further addition of CO. No flash.
I-133A	4.1	2.3	-	-	1.85	0.56	-	0.5	O_3 added to CO.
B	7.0	1.85	O_2, CO_2	-	1.75	0.62	-	0.1	More O_3 added.

TABLE 3 (CONTINUED)

RUN NO.	INITIAL PRESSURE OF REACTANTS (Torr)			FINAL PRESSURE OF COMPONENTS (Torr)			REACTANT PRESSURE DIFFERENCE		
	O_3	CO[1]	X[2]	O_3	CO	CO_2	ΔO_3	ΔCO	
I-135A	15.9	8.9	-	12.2	5.0	4.8	3.7	3.9	Silica gel purification of CO. No flash.
B	12.2	54	CO_2=4.8 O_2=4.0	<0.2	37	23	>12.0	17	Further addition of CO passed only thru N_2 trap. Flash.
I-137A	19.9	12.2	-	14.9	5.3	7.0	5.0	6.9	Silica gel purification of CO in both cases. No flash.
B	14.9	14.3	CO_2=7.0 O_2=6.0	11.6	11.8	10.3	3.3	2.5	
I-138	20.0	-	N_2=9.0	20.0	-	-	0.0	-	Nitrogen added to ozone.
I-139	20.7	6.3	-	17.8	2.5	5.3	2.9	3.8	Research grade CO in glass flask.
I-141	14.5	9.4	-	11.3	5.0	4.5	3.2	4.4	Additional L N_2 trap between manifold and reaction vessel.
I-153A	14.3	9.9	-	< 0.2	-	-	>14.1	-	Flash.
B	13.6	~1.2	CO_2=1.6 O_2=11.5	13.4	1.2	1.6	<0.2	0.0	Gas mixture absorbed on molecule sieve then added to O_3 in vessel. No flash.
C	13.4	8.0	CO_2=1.6 O_2=11.5	< 0.2	4.5	3.9	>13.2	3.5	Further addition of CO from tank, L N_2 trap. Flash.
I-155A	19.1	7.0	-	16.0	3.9	3.7	3.1	3.1	No flash. CO desorbed from charcoal slow addition.
B	15.8	25	CO_2=3.7 O_2=3.5	0.0	18.5	12.0	15.8	6.5	CO from tank, flash, adsorb mixture onto charcoal.
C	14.7	4.5	CO_2=3.0 O_2< 12	14.7	4.5	3.0	0.0	0.0	Desorb mixture from charcoal and add to O_3.
D	14.7	13.5	CO_2=3.0 O_2=<12	< 0.1	7.0	9.5	>14.6	> 6.5	CO from Tank, L N_2 trap, flash.

TABLE 3 (Continued)

RUN NO.	INITIAL PRESSURE OF REACTANTS (Torr)			FINAL PRESSURE OF COMPONENTS (Torr)			REACTANT PRESSURE DIFFERENCE		
	O_3	CO[1]	X[2]	O_3	CO	CO_2	ΔO_3	ΔCO	
I-163A	16.3	7.4	-	12.5	3.8	3.6	3.8	3.6	CO from tank, L N_2 trap add slowly, no flash.
B	12.5	3.8	O_2 = 3.6 CO_2 = 3.6 H_2 = 1.0	12.0	4.0	3.7	<0.5	0.0	Add 1 Torr of H_2.
C	12.0	3.9	O_2 = 3.6 CO_2 = 3.6 H_2 = 1.0 CH_4 = 1.4	6.6	3.0	3.9	5.4	0.9	Add 1.4 Torr of CH_4. Observe further slow decay of O_3 and CO. See Table 4.

1. Initial pressure of CO estimated from pressure differential observed in manifold when CO was expanded into reaction vessel.

2. X = other gas admixture.

First, various measures were taken to eliminate the inadvertent introduction of impurities. In all runs subsequent to run No. 101, the carbon monoxide tank was connected to the manifold through an all metal-glass junction, and the CO was fed through a liquid nitrogen cooled trap unless otherwise noted. Nevertheless, run Nos. 107, 111 and 113 showed no reduction in the rate of the reaction. In run No. 118 an effort was made to eliminate water from the system. For this purpose the oxygen used to generate ozone was passed through a silicagel drying column, followed by a U-tube immersed in liquid nitrogen. In addition the manifold and ozone generator line were baked at 120°C overnight. However, the initial rapid reaction remained. In run No. 114 it was attempted to slow the reaction by the addition of nitrogen to the carbon monoxide. Indeed, no chemiluninescence was observed in this experiment, but the reaction rate was not noticeably reduced.

Since carbon dioxide was a product of the reaction, it was of interest to determine its ability to inhibit the reaction. In run No. 115 a 1:1 mixture of ozone and CO_2 was prepared and CO was added to it. No inhibition of the reaction was observed. A similar experiment with oxygen was not undertaken because it was considered more meaningful to determine the inhibiting effect of a complete reactant product gas mixture. Run Nos. 128, 130 and several subsequent experiments were performed on this basis. The amount of carbon monoxide initially added to the ozone in the vessel was adjusted so that only a portion of the reactants were consumed. The decrease in reactant concentration and the concurrent CO_2 concentration increase were measured. Subsequently, additional carbon monoxide was added to the gas mixture in the reactor. In all such runs (128, 130, 135 and 137), the second addition of carbon monoxide caused the reaction to proceed further. These results strongly indicate that the initial rapid reaction is due to an impurity introduced with the CO, and at the same time the results demonstrate that neither CO_2 nor O_2, in the concentrations present, inhibit the observed chemical change. Run No. 133 further corroborates this conclusion. In this experiment the sequence of introducing reactants to the vessel was reversed, i.e., ozone was added to carbon monoxide. There was a negligible production of CO_2 and consumption of CO, when subsequently more ozone was added to the reaction mixture.

Having shown the presence of impurities in the CO, it was attempted in run Nos. 135 and 137 to purify CO by absorption on silicagel, which was outgassed by heating prior to the experiment. Carbon monoxide was absorbed at liquid nitrogen temperature and desorbed at dry ice temperature. Later in run No. 155, silicagel was replaced by charcoal as the absorber, which, similar to silicagel, absorbed CO at liquid nitrogen temperature and desorbed it at dry ice temperature. None of these experiments showed an abatement of the initial rapid reaction. Run Nos. 139 and 141 make evident that research grade CO obtained in a glass flask also results in a rapid initial reaction similar to the carbon monoxide drawn from the steel cylinder. Finally, it is shown in run No. 138, that the rapid decrease of ozone is not observed upon the addition of nitrogen, demonstrating that CO is a required reactant and that the impurity does not originate in the gas handling manifold.

Since the applied purification procedures had all failed to remove the impurity present in the carbon monoxide, it was attempted to utilize the reaction itself to clean up the carbon monoxide. Run Nos. 153 and 155 were performed accordingly. As previously, tank CO was first reacted with ozone in such a manner that very little ozone remained after the occurrence of the fast reaction. Subsequently, the reaction mixture was absorbed on either molecular sieve, or, more advantageously, on charcoal. Both absorbers had been outgassed prior to the experiments. More ozone was prepared and placed in the reaction vessel. The absorbed gas mixture was desorbed in the manifold. The desorption process was performed at $0^{o}C$ with molecular sieve and at dry ice temperature with the charcoal. In both cases a fractionation occurred, as expected, reducing the concentration of carbon dioxide, but not that of oxygen. The gas mixtures thus obtained were then added to the ozone in the reaction vessel. In both cases, no reaction was observed. When additional carbon monoxide from the tank was entered, however, the reaction occurred as usual, consuming most of the ozone in the process. These experiments show, in corroboration of the results of the other experiments discussed above, that the impurity is consumed in the reaction, and that the resulting gas mixture can be handled in the manifold without recontamination. It was not possible by the employed method of adsorption to free the purified CO from the reaction product oxygen, but the runs 153C and 155D demonstrate in addition to several of the other experiments discussed above, that oxygen does not inhibit the reaction, when tank CO is involved.

Although the experiments discussed so far leave no doubt that the carbon monoxide employed contains an impurity, they do not indicate the type of impurity involved. The analysis given by the supplier provides the following information: $H_2 < 5$ ppm; $O_2 < 10$ ppm; Ar < 10 ppm; $N_2 <$ 250 ppm; $CO_2 < 10$ ppm; total hydrocarbon content, as methane, < 2 ppm.* Clearly, the only impurities that could undergo an interaction with ozone are hydrogen or hydrocarbons. The adsorption - desorption experiments further indicate that the impurity must be rather volatile, since it survives the adsorption - desorption cycle. Thus, either hydrogen or methane are implicated. According to information by the supplier, the carbon monoxide used by us (the purest available on the market) is produced from methylformate. The final purification step is distillation at liquid nitrogen temperature, and the most likely impurities resulting from the procedures employed are hydrogen and methane. On the assumption that one or both of these impurities are involved, the final series of runs (163) were carried out for the purpose of determining whether hydrogen or methane are in fact responsible for the observed reaction. As usual, CO from the tank was first added to ozone in the reactor, to produce a stable gas mixture containing ozone and carbon monoxide. Subsequently, a small amount of hydrogen was added. The H_2 admixture did not produce a decrease of either ozone or CO, nor did it increase the

*A gas chromatographic analysis performed subsequently indicated that methane was present at a concentration of 0.9 ± 0.1 ppm.

CO_2 partial pressure. However, when a small amount of methane was added to this gas mixture, the reaction proceeded further. Both the concentrations of ozone and CO decrease, although the decrease of ozone was greater. Simultaneously, more CO_2 was formed. The reaction continued slowly during the next 20 hours, as shown in Table 4. This experiment thus indicates that methane (or a hydrocarbon impurity in methane) catalyzes the oxidation of CO by ozone. The observation that in this experiment the reaction is slow must be ascribed to the relatively large concentration of methane employed, compared to the rather small concentration present as impurity in carbon monoxide.

C. DISCUSSION

The results presented above, particularly those shown in Figure 2 demonstrate that the direct bimolecular reaction between ozone and carbon monoxide, presumed to proceed consecutive to the initial fast reaction phase catalyzed by the impurity, is negligibly slow at 23°C. From the maximum changes in ozone and carbon dioxide concentration shown in Figure 2 one can obtain an upper limit for the associated rate coefficient. Making use of the rate expression

$$-\frac{\Delta [O_3]}{\Delta t} = \frac{\Delta [CO_2]}{\Delta t} = k_6[CO]\ [O_3]$$

and inserting the observed change in ozone concentration, $\Delta[O_3]$, which is twice the upper limit change of CO_2, one obtains $k_6 \leq 4 \times 10^{-25}$ cc/molecule sec as the upper limit for the rate constant of reaction (6) at room temperature. This value is too small to effect a significant consumption of CO in the atmosphere when compared with the CO emission source strength. On the basis of the average atmospheric ozone concentration, 5×10^{11} molecules/cm^3, and the present CO concentration level of 0.1 ppm in the atmosphere, reaction (6) consumes less than 10^{-5} parts of the CO produced by anthropogenic combustion. On the other hand, the catalyzed initial reaction phase would be much more effective, since its rate is faster than the mixing time of the reactants. This aspect will now be discussed.

Figure 4 shows a plot of the amount of CO_2 formation versus the amount of CO consumed in each run. Despite the rather wide scatter, a straight line relationship is evident. The average rate $\Delta CO_2/\Delta CO$ is 0.98 ± 0.21. Within the experimental error this value is unity, which one would expect for an impurity catalyzed CO oxidation mechanism. The consumption of both ozone and carbon monoxide is a considerable fraction

TABLE 4

RESULTS OF EXPERIMENT I-163

TIME (min.)	PRESSURE OF REACTANTS AND PRODUCTS (Toor)				PRESSURE DIFFERENCES		
	O_3	CO	CO_2	CH_4	O_3	CO	CO_2
0	12.0	3.9	3.6	0	-	-	-
1	6.6	3.0	3.9	1.35	5.4	0.9	0.3
35	2.1	2.5	4.9	1.4	9.9	1.4	1.3
1050	1.2	-	-	-	10.8	-	-
1090	1.0	2.1	5.4	1.35	11.0	1.8	1.8
1135	0.8	1.8	5.3	1.30	11.2	2.1	1.7
1225	1.0	1.9	5.4	1.25	11.0	2.0	1.8

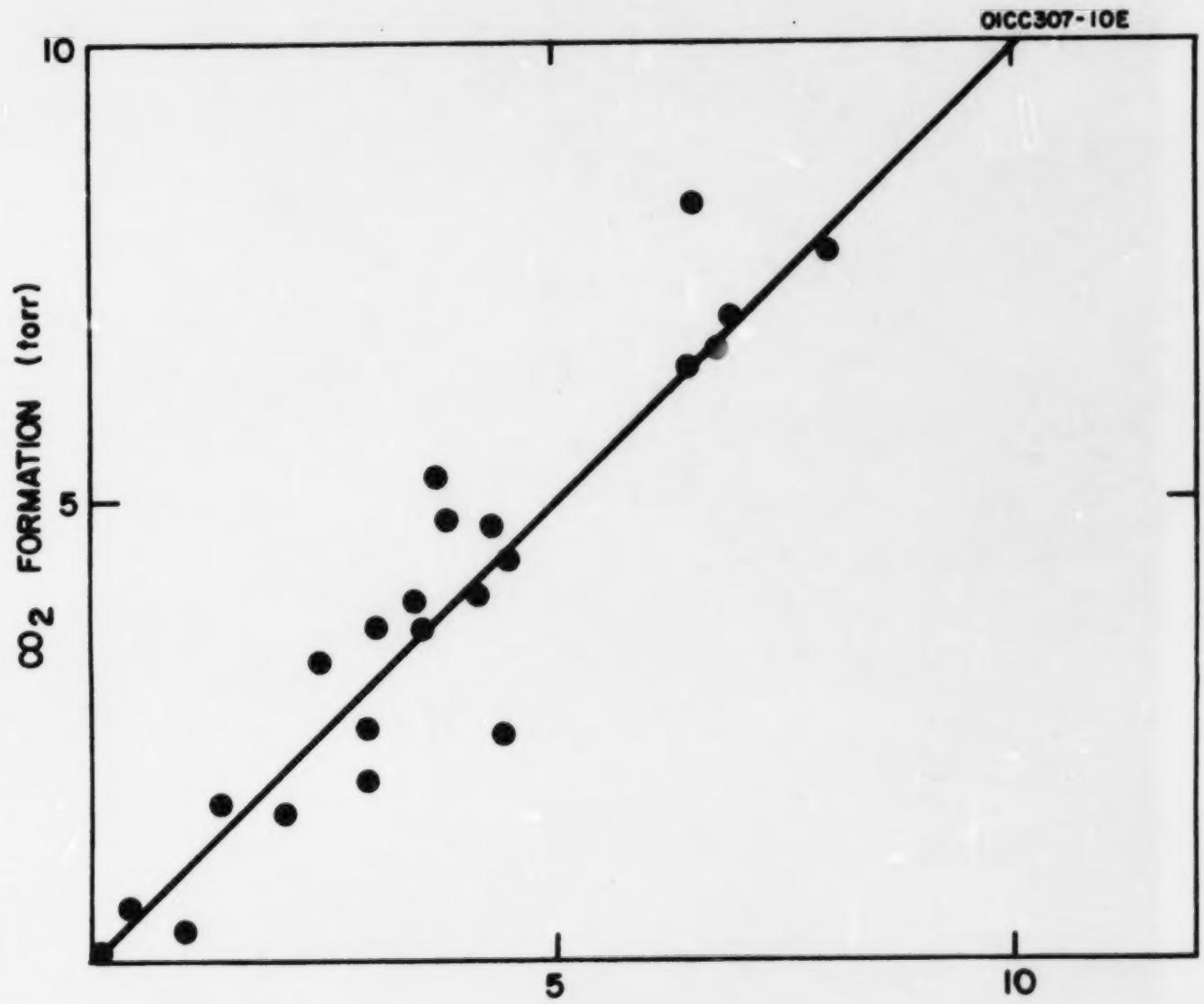


Figure 4. Relation of CO_2 formation versus CO consumption.

of the total initial reactant concentrations. The degree of consumption is much greater than the conceivable concentration of impurity. This factor, coupled with the speed of the reaction and the emission of light, indicates the occurrence of a chain reaction. Chain branching probably occurs, although the degree of branching cannot be too high, since no explosion was observed. In none of the experiments was the consumption of CO complete so that chain termination must also be effective in the reaction. Since the products of the reaction did not seriously inhibit it, and since in many runs ozone was not completely used up, it appears that the termination of the reaction is due mainly to the consumption of the impurity. Clearly, the detailed mechanism of the reaction cannot be specified on the basis of the available data, but some qualitative features are made apparent.

Figure 5 shows that the consumption of ozone increases with increasing addition of carbon monoxide. At reactant concentration ratios less than unity the consumption is about 40 percent of the amount of CO admixed, but at initial concentration ratios greater than unity the probability of O_3 decomposition rises steeply, so that above $[CO]_o/[O_3]_o = 1.5$ essentially all the ozone is depleted. Note, that the flagged points indicate the second addition of fresh CO, and that only the concentration of the additional CO was used in calculating the initial reactant concentration ratio, because only this portion represents the further addition of impurity. Since the amount of impurity introduced to the reaction vessel must be proportional to the added CO concentration, the data in Figure 5 suggest a thermal decomposition of O_3 in addition to its consumption in the CO oxidation reaction, as the impurity - ozone concentration ratio is increased and the reaction grows more violent. In this respect it is noteworthy that a very slow addition of CO to the ozone in the reaction vessel controls the thermal decomposition of O_3 apparently because the heat generated by the catalyzed oxidation of CO is then carried to the surroundings more effectively. Also indicative of an appreciable decomposition of ozone is the accompanying flash of light, which was absent only when the CO reactant was admixed very slowly, or at low CO/O_3 reactant concentration ratios. Figure 5 demonstrates that the probability of light emission increases with the percentage decomposition of ozone. It appears that at high CO/O_3 reactant ratios the ozone decomposition is mainly thermal in nature. This conclusion is further supported by the observation that the ozone decomposition exceeds the formation of CO_2 product and the depletion of CO reactant. In Figure 6 are plotted the ratios $\Delta O_3/\Delta CO_2$ and $\Delta O_3/\Delta CO$, to show that these ratios increase as the initial CO/O_3 reactant ratio increases. At sufficiently small initial reactant ratios, the consumption of ozone equals the consumption of CO and the formation of CO_2, i.e. the ratios $\Delta O_3/\Delta CO$ and $\Delta O_3/CO_2$ approach unity. In conjunction with Figure 4 this fact then indicates that the catalytic CO oxidation is stoichiometric, and one ozone molecule is consumed for each CO molecule oxidized to CO_2.

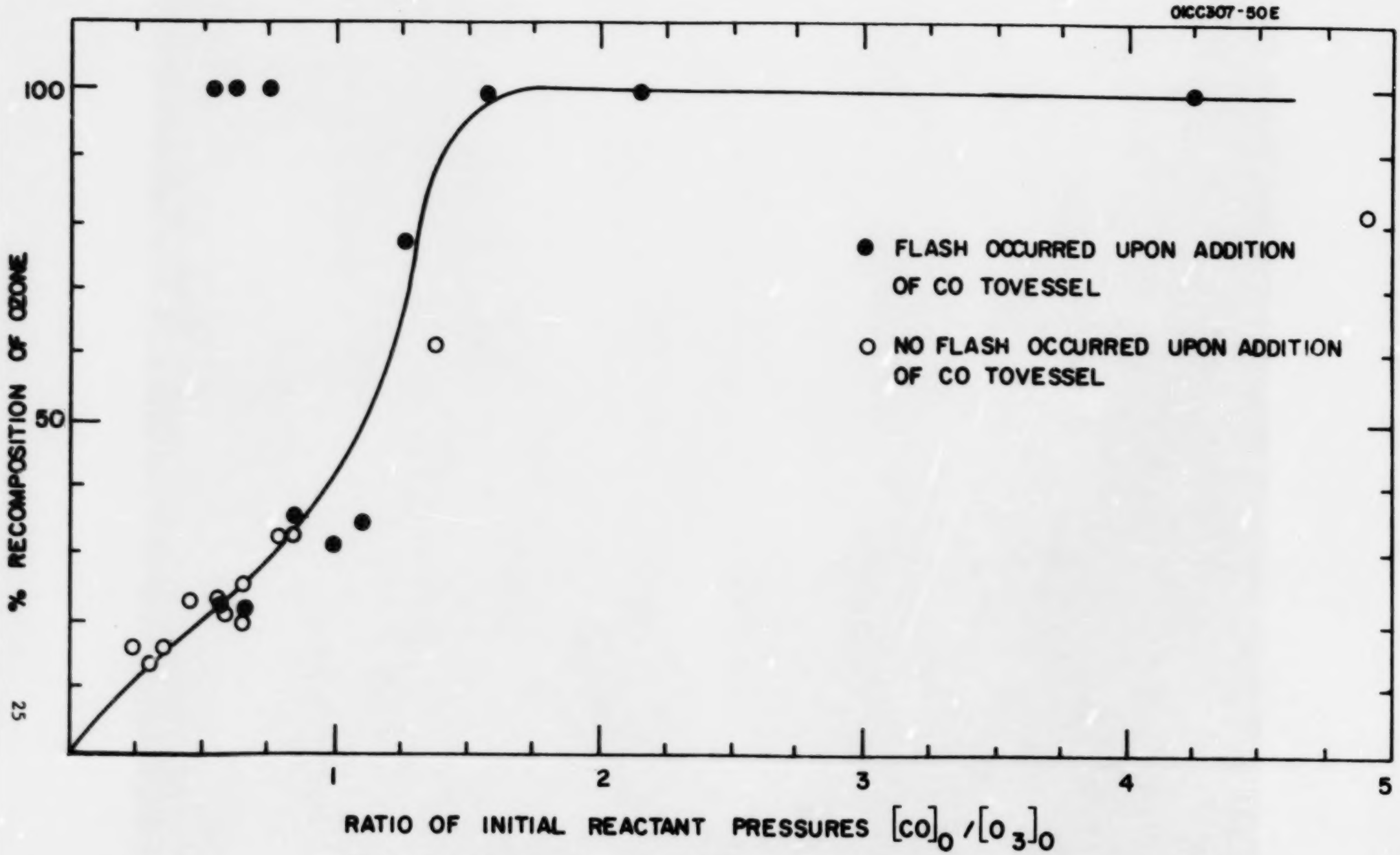


Figure 5. Percent ozone consumption as a function of reactant pressure ratio. Flagged points indicate second addition of CO.

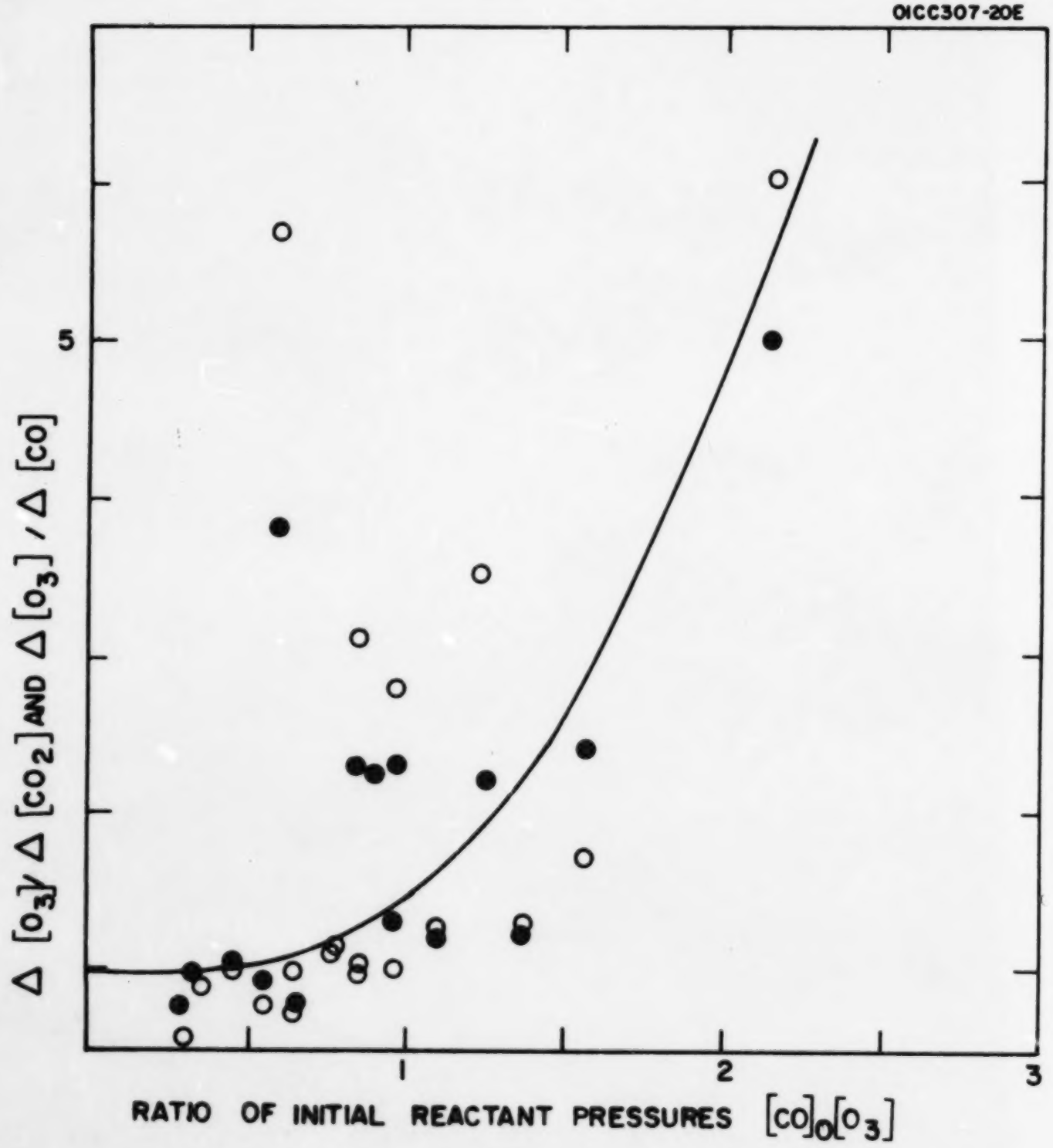


Figure 5. O_3 consumption versus central reactant ratio $[CO]/[O_3]$. Open circles: $\Delta O_3/\Delta CO_2$; filled circles $\Delta O_3/\Delta CO$. Flagged points indicate the second addition of CO.

It has already been mentioned that the termination of CO oxidation after the initial rapid reaction indicates an essentially complete consumption of the impurity which catalyzes this reaction. Since the chain carrier responsible for the CO oxidation must derive from the impurity by its interaction with ozone or an O_3 decomposition product, the amount of CO_2 formation and the reactant depletion should be proportional to the initial concentration of impurity, which in turn is proportional tc the pressure of fresh CO admitted to the reaction vessel. Figure 7 shows that this is the case. Only those data are used in which the O_3 decomposition is not appreciably in excess of the formation of CO_2, and the amount of CO_2 formation as well as the consumption of both CO and ozone are plotted versus the pressure of fresh CO admixed to the reactant in the vessel.

To account for the sum of these features it is suggested that the catalyzed CO oxidation is accomplished by the chain mechanism

$$(1) \quad OH + CO \rightarrow CO_2 + H$$

$$(7) \quad H + O_3 \rightarrow OH + O_2$$

At temperatures near 300°K the second of these reactions is much faster than the first, so that the OH radical concentration is kept at a stationary value. The production of CO_2 is then given by the rate

$$\Delta CO_2/\Delta t = k_1 [OH] [CO]$$

where $k_1 = 2 \times 10^{-13}$ cc/molecule sec is the rate coefficient associated with reaction (1) and the time scale Δt is taken to be 1 sec, corresponding to the approximate mixing time of the reactant. From the data in Figure 7 one derives an average OH radical concentration necessary to obtain the observed CO_2 production, of about 2×10^{12} molecules/cc.

Since it has been shown that methane is a likely impurity, we now compare the required stationary OH radical concentration with that produced during the same time period by the interaction between ozone and methane. Two mechanisms are probable; one involving oxygen atoms and the other proceding is a direct interaction of ozone with methane. In the first case oxygen atoms are formed from ozone (Benson and Axworthy, 1965) via the reactions

$$(8) \quad M + O_3 \rightarrow O_2 + O + M$$

$$(9) \quad O + O_3 \rightarrow O_2 + O_2$$

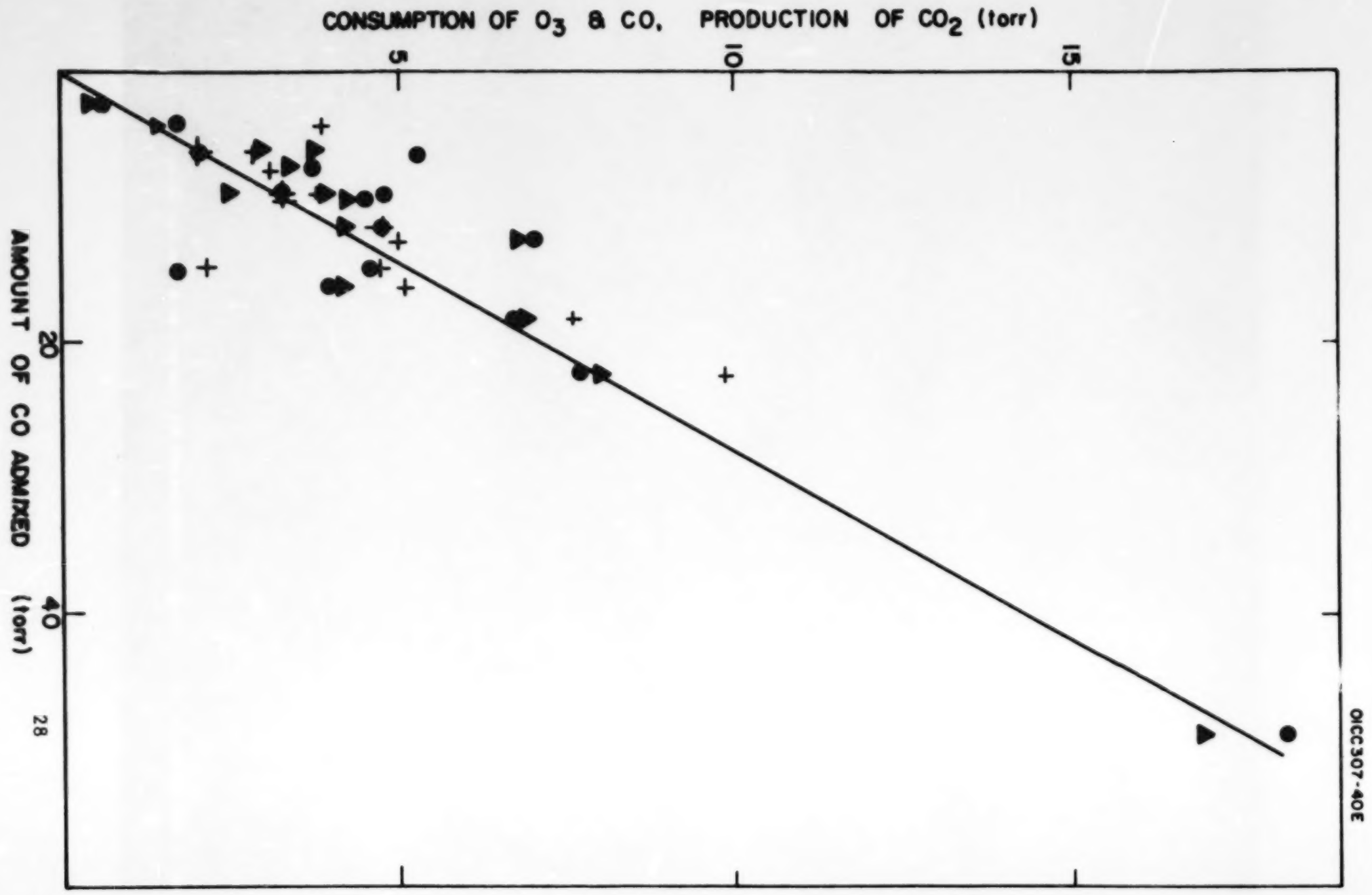


Figure 7. Consumption of O_3 (+), consumption of CO (▲) and production of CO_2 (●) versus amount of CO admitted to the reaction vessel.

where M is either ozone or carbon monoxide, and the stationary oxygen atom concentration resulting therefrom is

$$[O] = \frac{k_8}{k_9} [M] = 2 \times 10^{-10} [M].$$

Here the values for $k_8 = 7.5 \times 10^{-25}$ cc/molecule sec and $k_9 = 3.7 \times 10^{-15}$ cc/molecule sec at room temperature are inserted. The reaction with methane

$$(10)\ O + CH_4 \rightarrow OH + CH_3$$

has the room temperature rate coefficient $k_{11} = 1 \times 10^{-16}$ cc/molecule sec. Assuming a concentration of (M) = 5×10^{17} molecules/sec, and a methane concentration of 1 ppm or 0.5×10^{12} molecules/cc, the rate of OH formation by reaction (10) is

$$\frac{\Delta[OH]}{\Delta t} = 10^{-16} \times 2 \times 10^{-10} [M] [CH_4] \approx 10^4 \frac{\text{molecules}}{\text{cc sec}}$$

In the second case of a direct interaction between ozone and methane

$$(11)\ O_3 + CH_4 \rightarrow \text{product}$$

use is made of the rate coefficient derived by Dillemuth, et al (1960): $k_{11} = 2.4 \times 10^{-14} \times \exp(-13{,}900/RT)$, which at room temperature provides the maximum possible rate of OH formation.

$$\frac{\Delta[OH]}{\Delta t} = 1.5 \times 10^{-24} [O_3] [CH_4] \approx 7 \times 10^5 \frac{\text{molecules}}{\text{cc sec}}$$

It is apparent that both mechanisms cannot provide the OH concentration needed to oxidize with CO within the available time interval of at the most a few seconds. A branching chain mechanism is definitely required. In this respect, it is of interest to note that Dillemuth, et al (1960) in studying the ozone-methane reaction, observed explosions unless the methane concentration was in excess over that of ozone. The occurrence of an explosion strongly suggests that a branched chain mechanism is involved.

From the present experimental results it is concluded that methane is strongly implicated as the impurity responsible for the catalyzed CO oxidation, even though the effect of another hydrocarbon cannot be entirely precluded. Methane and/or other hydrocarbons are present in the atmosphere in small concentrations ($[CH_4] \approx 1$ ppm) so that a catalytic oxidation of CO in this manner by ozone is a likely process. Clearly, at atmospheric pressures and with the low atmospheric concentration levels of both methane and CO, the rates would be drastically reduced from those observed in the present laboratory experiments, and it is questionable whether a branching chain process can be maintained. The experiments by Harteck and Dondes (1957) at the lower temperatures may be interpreted in this way and can provide an estimate for the rates to be expected.

It can be shown that the associated CO oxidation rate suffices to provide a significant sink for CO in the troposphere. Thus, while the direct bimolecular oxidation of CO by ozone has been found here to be too slow to provide a significant CO removal path in the atmosphere, one cannot at the present time exclude the hydrocarbon catalyzed CO oxidation from consideration. Quantitative conclusions on this aspect are precluded because of the present uncertainty of the associated mechanism.

IV. CO OXIDATION IN THE HYDROSPHERE

A. INTRODUCTION

In addition to the atmosphere, the oceans provide a considerable reservoir of oxygen. Since the solubility of carbon monoxide in seawater is about the same as that of oxygen and nitrogen, and since seawater generally is an oxidizing environment, CO oxidation in the oceans provide a conceivable path for the removal of CO from the atmosphere. Although recent expeditions in the Atlantic (Swinnerton, et al, 1969; Seiler and Junge, 1969) have shown that biological activity close to the surface of the oceans can be a source of CO, it was nevertheless of interest to explore the possibility of CO oxidation in aqueous solution. Such a process would have to be essentially catalytic in nature. The active catalyst could fall into three groups: cationic, anionic, or suspended matter, such as colloids. Since the catalyst need not be present in a particularly high concentration, and the oceans are endowed with almost all elements in one form or another, a truly comprehensive study could not be made in the present program. In view of the rather extensive sedimentary depositions in the open seas and high catalytic activity of the ferromanganese minerals of which the sediments are composed, a heterogeneous catalysis with freshly precipitated, colloidal iron hydroxide was considered a probable path of CO oxidation, worthy to be explored. However, the experiments did not indicate this catalyst system to be sufficient for a CO oxidation. Instead, simple sodium chloride, dissolved in water in the concentrations normally found in seawater appeared to promote the interaction of CO with the solution much more rapidly.

B. EXPERIMENTAL

The experimental arrangement used to study the CO oxidation in aqueous solution is sketched in Figure 8. The central part of the apparatus is a cylindrical reaction vessel of about 100 cc volume, which is attached to the rest of the system via a tapered joint. A side arm accomodates a pH electrode. The gas mixture is circulated through the solution by means of a peristaltic pump. An impinger breaks the gas into bubbles of sufficiently small size so, that intimate contact with the solution occurs. The system is joined to a gas handling manifold, which can be evacuated by a small mechanical pump. Cold traps are provided in order that impurities in the added gases can be minimized.

Any oxidation of carbon monoxide will lead to the formation of CO_2. This product will only partially exist in the gas phase, as it is dissolved in the solution with the formation of bicarbonate according to the reaction

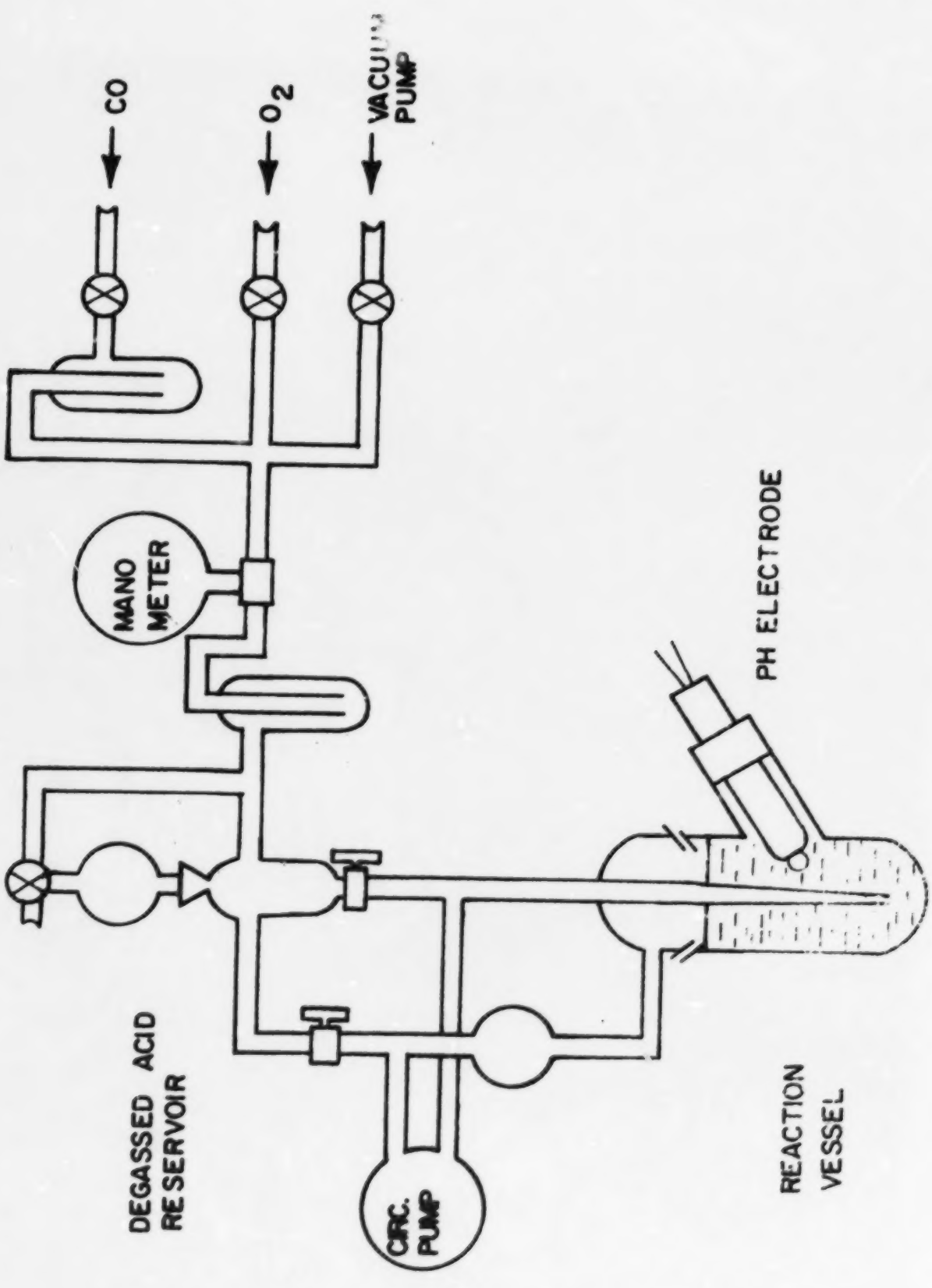


Figure 8. Apparatus for the Investigation of CO Oxidation in Aqueous Solution

$$CO_2 + OH^- \rightarrow H\,CO_3^- \qquad (12)$$

Since the consumption of OH^- must be accompanied by an increase in proton concentration (unless the solution is buffered), a decrease in pH is expected to occur in the presence of CO_2 formation. The main analytical test, therefore, was the measurement of pH changes of the solution.

A degassed acid reservoir was incorporated into the apparatus for the purpose of acidifying the solution and bringing the dissolved product CO_2 into the gas phase for external analytical detection. However, it was not used in the experiments described below. The pH electrode was connected to a standard pH meter whose output was coupled to a strip chart recorder via the circuit shown in Figure 9. This auxiliary device allowed adjustment of the recorder pen to the center of the scale at pH = 7.0, with a range of ΔpH = 1 per ten chart divisions. The pH electrode, meter and recorder combination was calibrated by means of standard buffer tablets available commercially. The system was checked for drifts and irregularities by means of a second pH meter and was found to operate satisfactorily.

The adopted experimental procedure was as follows. The desired solution was prepared and placed in the reaction vessel. The system was degassed for about 15 minutes by evacuation with the mechanical pump. Subsequently, the valve leading to the pump was closed and carbon monoxide was entered from a storage tank, passing the gas through a liquid nitrogen cooled trap. The partial pressure was adjusted to 300 Torr. The stop cock leading to the system was then closed, the manifold was evacuated again, and oxygen was bled into the manifold at a pressure greater than 300 Torr. The stopcock leading to the system was opened, more oxygen was introduced until the total pressure was approximately 730 Torr, and the stopcock was closed. The pH was registered, and circulation of the gas mixture was initiated. In some runs, nitrogen was substituted for oxygen or carbon monoxide.

C. RESULTS

Experiments were performed over a period of at least 20 hours. The number of runs performed, the kind of solutions employed and the pH changes registered are listed in Table 5. In all cases the temporal pH behavior was characterized by the following pattern. An initial rise from pH = 5 to pH = 7 occurs during the outgassing of the solution prior to the experiment. When the apparatus is charged with the gas mixture and the circulating pump switched on, the pH decreases rapidly within a time period of 2-15 minutes, indicating a reasonably fast equilibration of the gas mixture with the solution. The size of the initial pH decrease varied but rarely exceeded one unit. Subsequently, a slow pH change occurs for at least ten hours. However, in some runs no subsequent slow pH change was observed. The individual runs may now be discussed.

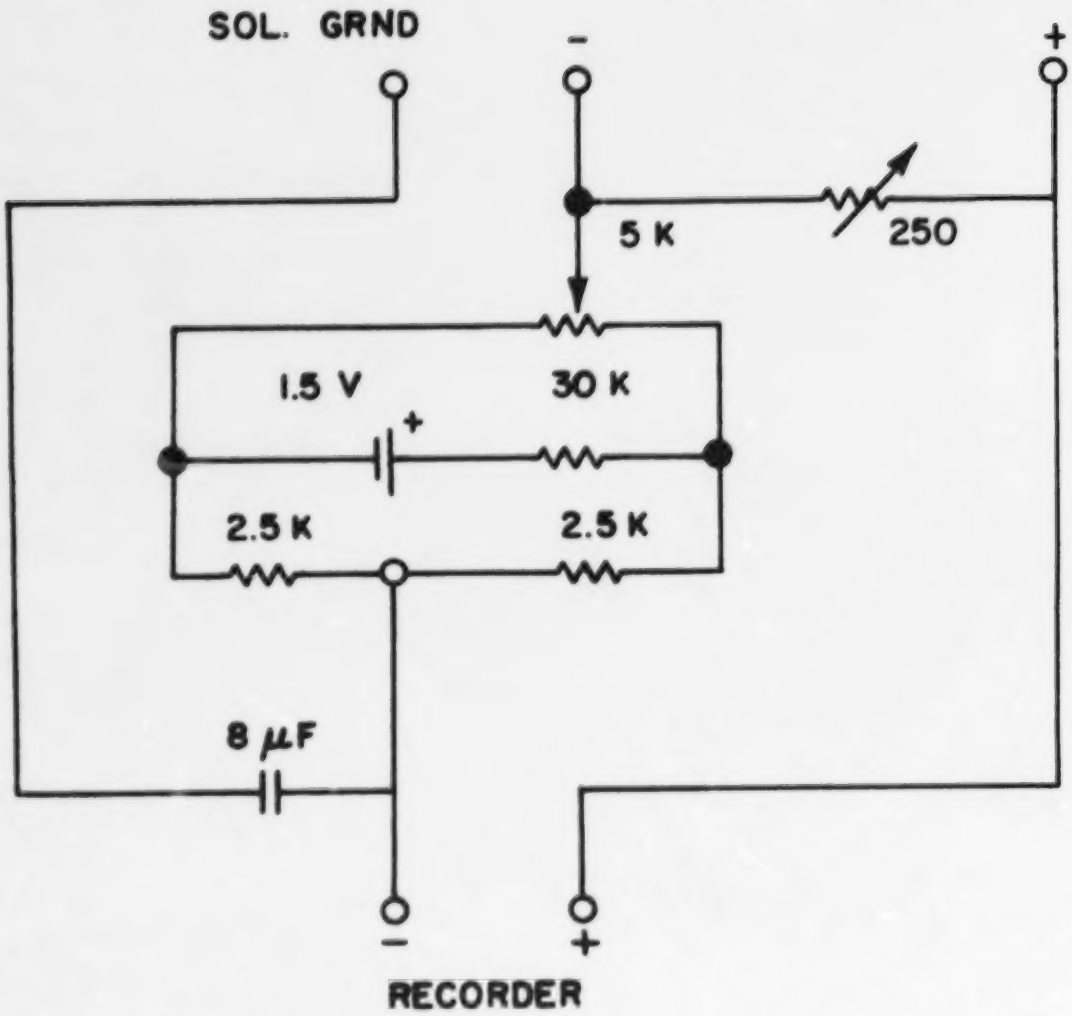


Figure 9. Circuit for matching recorder to pH meter.

TABLE 5

RUN NO.	GAS MIXTURE	REAGENT	pH (AT START)	pH (20 HRS)	INITIAL ΔpH
1	CO/O_2	H_2O	7.0	5.7	
2	"	"	6.4	5.2	-0.6 after 15 min
3	"	"	6.8	5.5	-0.7 after 5 min
4	"	$FeCl_3$ buffered[1] with Na OH	7.0	6.1	-0.2 after 5 min
5	"	"	7.2	7.2	no change
6	"	$Fe_2(SO_4)$ buffered[2] with Na OH	7.3	7.1	+0.2 after 2 min
7	"	"	6.9	4.2	-0.3 after 15 min
8	"	Na Cl [3]	6.9	3.3	-1.0 after 2 min
9	"	"	7.85	3.3	-1.9 after 2 min
10	N_2/O_2	"	7.3	4.9	-1.1 after 10 min
11	N_2/CO	"	7.8	6.1	-1.4 after 15 min
12	CO/O_2	"	7.2	4.0	-1.2 after 2 min
13	N_2/O_2	"	7.0	6.0	-1.0 after 5 min

1 0.0147g/1 = 0.00009 mole/liter

2 0.0384g/1 = 0.00009 mole/liter

3 18.98g/1 = 0.325 mole/liter

Initially, the effect of distilled water was tested. In this system no pH change is expected beyond the initial drop due to equilibration of the system. Nevertheless, a decrease of $\Delta pH = 0.6$ is observed over a period of 20 hours in addition to the initial pH change, indicating the occurrence of a minor reaction. In run Nos. 4 through 7 iron hydroxide was produced by dissolving trivalent iron in the form of either iron chloride or iron sulfate in distilled water in the concentrations reported as characteristic for the open seas. The resulting solutions were rather acidic ($pH \approx 3.0$) so that sodium hydroxide was added to provide an initial pH value of about 7.0. With exception of run No. 7, which produced a considerable pH decrease, the changes observed in the colloidal iron hydroxide system were smaller than in distilled water alone. These results thus indicate the iron in the form used does not promote the oxidation of CO, although it should be noticed that the involved concentrations were rather small. Much more drastic changes were observed in the subsequent runs in which the sodium chloride solutions were employed, in concentrations similar to that found in seawater. These experiments are characterized by initial decreases of pH larger than in the preceding runs, which brings the pH value to about $pH = 6.0$. In the presence of both oxygen and carbon monoxide the pH then decreases to less than $pH = 4.0$ within 20 hours. By comparison, the relative small change in the first seven runs indicates that the pH decrease observed with the sodium chloride solutions is a genuine effect of this solute system. It was desirable to check whether the change could ensue from either CO or oxygen alone. For this purpose, carbon monoxide was replaced by nitrogen in run No. 11. In run Nos. 11 and 13, the pH change observed subsequent to the initial rapid drop was negligible and in run No. 10, while not completely negligible, it was still much less than than encountered when both carbon monoxide and oxygen were present. These results thus evidence clearly that both oxygen and carbon monoxide are required for the observed effect. The observation that carbon monoxide along does not produce a pH decrease also rules out that the effect is due to the formation of sodium formate, a product known to be formed when carbon monoxide interacts with water. Tentatively, it may be assumed, therefore, that the pH decrease is due to the formation of bicarbonate following the catalytic oxidation of CO. The pH change can be expressed as an increase in hydrogen ion concentration which must be equal to the decrease of hydroxyl ions consumed in the process. As an example, Figure 10 shows the increase in H^+ ion concentration versus time as observed in run No. 9. An almost linear relationship is apparent. The rise in H^+ ion concentration observed in run Nos. 8 and 12 likewise was linear with time, although by about a factor of two smaller. Also shown in Figure 10 is the increase in H^+ ion concentration observed in run No. 10, which showed the greatest change in the absence of CO, to demonstrate the magnitude of the effect arising from the catalytic interaction of CO and oxygen.

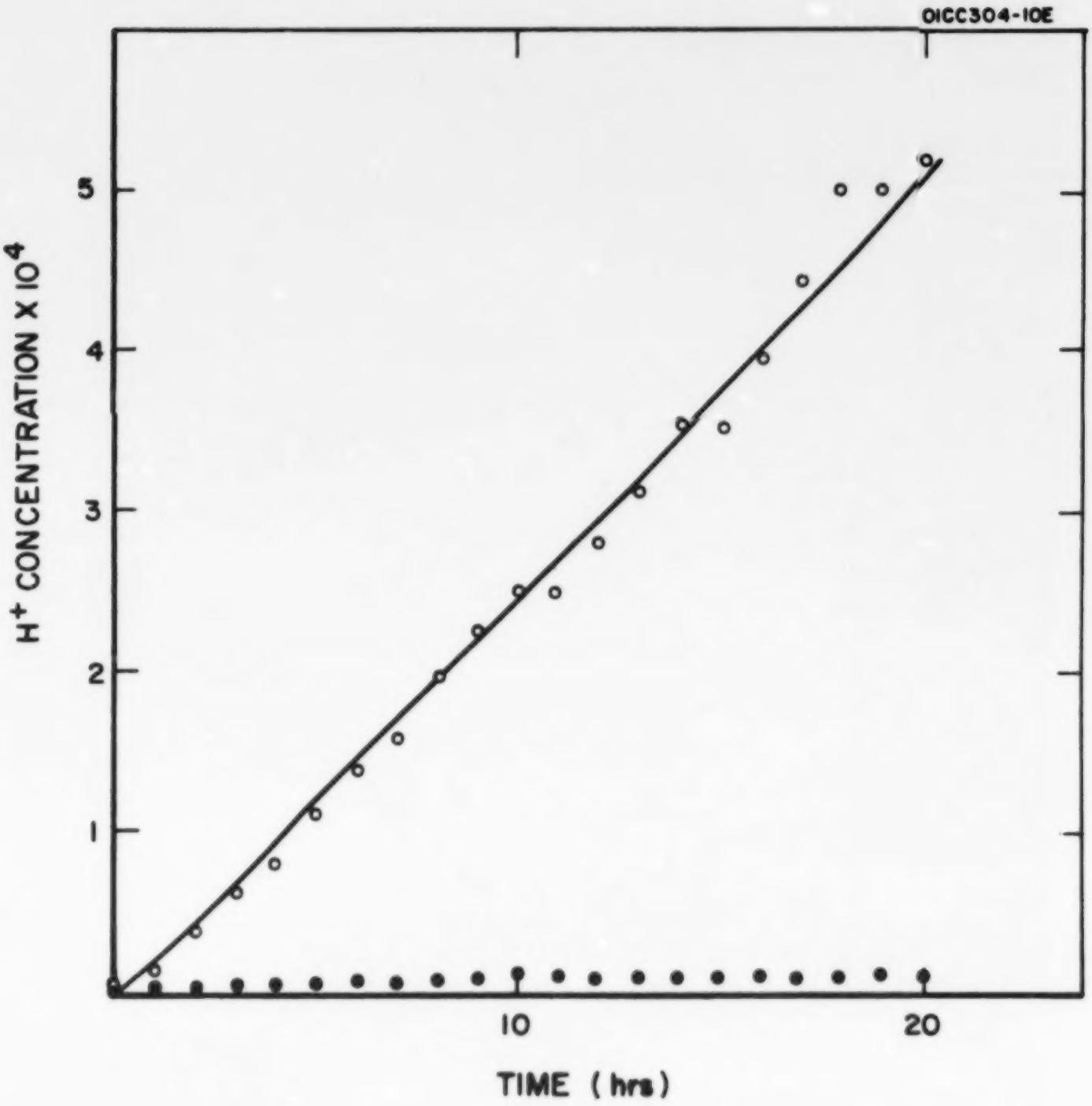


Figure 10. Increase in hydrogen ion concentration with time upon bubbling CO - O_2 mixture (O) or N_2 - O_2 mixture (●) through a 0.32 molar NaCℓ solution.

D. CONCLUSIONS

The present exploratory study has demonstrated that a process involving both CO and oxygen in the presence of sodium chloride in aqueous solution produces an appreciable lowering of the pH. This process does not appear to involve the production of formate from dissolved CO, since it requires the presence of oxygen. The working hypothesis has been to assume that the pH decrease is due to the oxidation of CO to carbon dioxide. Clearly, no verification of this hypothesis has been made, but at the present state, it is not possible to suggest an alternative explanation for the observations. Because of this uncertainty, possible mechanism for the process will not be discussed, but it should be noted that if the decrease of pH is due entirely to CO_2 formation, the rate of CO oxidation would suffice to have the oceans consume an appreciable portion of the anthropogenic carbon monoxide, provided the rate here observed is maintained in the presence of other ions found in the oceanic environment besides sodium and chloride.

Recent oceanic sampling data have shown (Swinnerton, et al, 1969; Seiler and Junge, 1969) that the oceans are a source of CO rather than a sink, with a source strength roughly equalling that from combustion processes. Obviously, in spite of possible aqueous CO-oxidation there exists a net balance production. In view of this new information, it does not appear very promising at the present time to continue investigations into the catalytic oxidation of CO in seawater in comparison to other potential CO removal processes.

V. GENERAL CONCLUSIONS CONCERNING SINKS FOR CO IN THE ATMOSPHERE

The present investigation has aimed at the identification of sizable sinks for CO in the atmosphere and the hydrosphere by first identifying promising CO removal processes, then studying them in the laboratory to evaluate the associated rates of CO removal. In this manner their significance with regard to the removal of CO from the atmosphere can be determined. Three processes were considered: depletion of CO in the stratosphere, oxidation of CO by ozone in the troposphere, and oxidation of CO in the hydrosphere. In the first case sufficient auxiliary information was available for a theoretical evaluation of the stratosphere as a CO sink. Concerning the reaction of CO with ozone, some previous experimental data were contained in the literature, but they were insufficient to make the necessary assessment, so that a laboratory study became necessary. With regard to the third case, oxidation of CO in the hydrosphere, the available information was so scant, that an exploratory experimental study was desirable which would provide a rough indication of the feasibility of such a process.

The results of these investigations contained in this report make apparent that none of the considered processes can account singly for the total CO sink required if the presently known rate of CO emission is to be balanced by an equivalent removal rate. Rather, it appears that several processes contribute. One such process is the oxidation of CO in the stratosphere, as shown in Section II. Even though essentially all the CO entering the stratosphere through a tropopause is destroyed, this sink consumes only 11-15 percent of the total tropospheric CO inventory per year, because it depends on the limited rate of transport of CO rich air from the troposphere to the stratosphere.

The oxidation of CO by ozone in a direct bimolecular reaction has been shown here to be immeasurably slow, so that it does not contribute to CO removal in the troposphere. However, the oxidation of CO by ozone was found to be catalyzed by methane, even if present in very small concentrations. Since methane is an atmospheric constituent, a route of CO removal is opened up. This process has been shown to occur by a chain reaction, presumably involving OH radicals. However, its mechanism, particularly under tropospheric conditions, is uncertain, and further investigations will be required in order to determine the applicable CO removal rate. At the present time, the CO oxidation in the troposphere by methane catalyzed ozone reaction appears to be a promising atmospheric sink for CO, but its significance cannot yet be fully assessed.

Finally, owing to the possibility of CO oxidation in the hydrosphere, a series of exploratory experiments were performed which indicate that the catalytic oxidation of CO in aqueous sodium chloride solutions appear to occur with a rate sufficient for the oceans to constitute a sizable CO sink. While the results obtained certainly require additional confirmation of this conclusion, and the details of the reaction mechanism have

not been studied, there is recent information according to which the oceans constitute a net source of CO rather than a sink due to biological processes. Thus, if salt water catalyzes the oxidation of CO, the residence time of carbon monoxide in the seas must be insufficient to effect an appreciable removal of this natural source, so that a considerable portion is emitted into the atmosphere.

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